# PERKIN'S REACTION.

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THE

# ACTION OF SALICYLIC ALDEHYDE

ON

# SODIUM SUCCINATE

IN PRESENCE OF ACETIC ANHYDRIDE.

## Inaugural Dissertation

SUBMITTED TO

THE FACULTY OF MATHEMATICS AND NATURAL SCIENCES OF THE KAISER WILHELM UNIVERSITY, STRASSBURG,

FOR

THE ACQUISITION OF THE DOCTORATE.

BY

G. DYSON,

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The following investigation was carried out in the "Kaiser-Wilhelms-Universität," Strassburg.

I take the present opportunity of thanking Professor Fittig for the valuable advice he has so generously given me whilst engaged upon this work, and also for his kindness to me during my stay in Strassburg.

# Introduction.

PERKIN,* in 1877, whilst working on the synthesis of Coumarine, discovered a new method for the preparation of unsaturated acids. This method consisted in allowing an acid anhydride to act upon a metallic salt and an aldehyde at a high temperature.

It is not easy to understand the different stages of this reaction, and the question, as to whether the reaction takes place between the metallic salt, or the anhydride and the aldehyde, has given rise to a most interesting discussion.

Perkin holds the latter view; whilst Fittig, who with his pupils has investigated this subject most carefully, asserts that when the temperature at which the reaction is carried out is not too high, the reaction only takes place between the aldehyde and metallic salt.

This view Stewart† has proved to be correct by the synthesis of isophenyl-crotonic acid, which he obtained by acting on a mixture of benzaldehyde and sodium isosuccinate, at the ordinary temperature, with acetic anhydride; in this reaction no trace of cinnamic acid was formed.

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* Jour. Chem. Soc., 1877, Vol. i., p. 388.

† Jour. Chem. Soc., 1883, p. 403.

Fittig explains the reaction in the following manner. In the first place he assumes the formation of an unstable oxy-compound, which is immediately decomposed into the more stable unsaturated acid and water; quite analagous to the formation of aldol by the condensation of two molecules of aldehyde. The following example will serve to illustrate my meaning more fully:—

I. $C_6H_5CHO + CH_3COOH = C_6H_5 - CHOH - CH_2COOH$

$C_6H_5CHOH - CH_2COOH = C_6H_5 - CH = CH - COOH + H_2O$

This assumption has since been justified by the preparation, by Jayne,* of phenyl-hydroxypivalic acid, obtained by the action of acetic anhydride on a mixture of benzaldehyde and isobutteric acid.

In order to see if Perkin's reaction is equally applicable to the oxyaldehydes I undertook, at the request of Professor Fittig, to investigate, whether by the action of sodium succinate on salicylic aldehyde analogous compounds could be obtained to those yielded by acting on benzaldehyde with the same salt.

Jayne† has shown that by acting on sodium succinate with benzaldehyde, at a temperature of 100—120° C., the principal product of the reaction is phenyl-paraconic acid $C_{11}H_{10}O_4$.

It was, therefore, to be expected that by substituting

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* Ann. d. Ch. 216, p. 115.

† Ann. d. Ch. 216, p. 97.

salicylic aldehyde for benzaldehyde oxyphenyl-paraconic acid would be formed. This expectation was not realised; on the contrary, in place of an acid a perfectly neutral body was obtained, which subsequent investigation proved to be dicoumarine $C_{18}H_{10}O_4$.

Zwenger* had in 1872 shown that coumarine treated in aqueous solution with sodium amalgam, care being taken that the coumarine is not present in excess, gives mililotic acid $C_9H_{10}O_3$; when he acted with sodium amalgam on an excess of coumarine in alcoholic solution the reaction, however, proceeded quite differently; in this case he obtained the sodium salt of a new acid, which he called Hydrocoumaric acid $C_{18}H_{18}O$ The characteristic properties of this acid are, that it forms a sodium salt practically insoluble in alcohol, and that on heating it gives off two molecules of water, forming an anhydride melting at 222°C.

Cohen,† by reduction of $\beta$ methyl umbelliferon-p-methyl ether, in alcoholic solution with sodium amalgam, obtained a compound $C_{22}H_{22}O_6$, which he considered belonged to the same class of bodies as Zwenger's acid. As the above-mentioned compounds are the only dicoumarines yet known, it seemed desirable that the dicoumarine obtained by the action of salicylic aldehyde on succinic acid should be submitted to a thorough investigation.

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* Ann. d. Ch., Sup. B. 8, p. 32.
† Inaugural Dissertation, München, 1884.

## On the Action of Salicylic Aldehyde on Sodium Succinate.

A MIXTURE of salicylic aldehyde, sodium succinate,* and acetic anhydride, in the proportions indicated by their respective molecular weights, was heated in a flask connected with an inverted condenser, on a water bath, for 24 hours. It is essential to the success of the experiment, that every trace of moisture be excluded from the apparatus, and that all the material used be perfectly dry. After the heating on the water bath had been proceeded with for the specified time, the contents of the flask, which had darkened considerably in colour, were treated with hot water, in order to remove the sodium succinate and acetic anhydride that still remained unacted upon; the excess of salicylic aldehyde was next removed by distillation in a current of steam. The residue, after washing with ether to remove a tarry substance which is always formed in small quantity, consisted of a light yellow crystalline powder, insoluble in all ordinary solvents.

It was recrystallised from hot glacial acetic acid, in which it is only sparingly soluble; on cooling it separated

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* To ensure that the sodium succinate, used in these experiments, was perfectly dry, it was heated in an air bath at 140° C. for four hours.

out in needle-shaped crystals. The analysis of this compound showed it to have the composition $C_{18}H_{10}O_4$; it is formed by the condensation of two molecules of salicylic aldehyde with one of succinic acid and has been called dicoumarine.

The above method did not yield satisfactory results, as the greater part of the aldehyde remained unacted upon; the following modification was therefore tried, and as it proved to be much better it was adopted for the preparation of all the material used in this research.

A mixture of 10 grammes sodium succinate, 15 grammes salicylic aldehyde, and 13 grammes acetic anhydride, was heated in a sealed tube for 40 hours at a temperature of 140° C. The contents of the tube were then extracted with hot water, and the residue, which consisted of dicoumarine and unaltered salicylic aldehyde was treated in exactly the same manner as described under the former process.

From 10 grammes of salicylic aldehyde about 5—6 grammes of dicoumarine were obtained.

It was found that an excess of acetic anhydride did not increase the yield of dicoumarine but gave rise to the formation of various complicated condensation products, which have not been further investigated. The dicoumarine was purified by recrystallisation from hot glacial acetic acid; the product thus obtained was slightly yellow, and it was found impossible to obtain, by this method of purification, á perfectly colourless body. It can, nevertheless, be completely decolourised, by dissolving in hot caustic soda and reprecipitating again by the addition of hydrochloric acid; this process will be more fully described later on.

The melting point of dicoumarine lies above 330° C. On fusing it with caustic soda, salicylic acid is formed.

The following are the analytical results obtained :—

I. 0·2012 grammes of substance gave 0·5522 grammes of $CO_2$ and 0·0650 grammes of $H_2O$.

| Calculated for $C_{18}H_{10}O_4$. | Found. |
|---|---|
| C=74·48 % | C=74·84 % |
| H= 3·45 % | H= 3·54 % |

II. Analysis (after being recrystallised again):—

0·285 grammes of substance gave 0·7775 grammes of $Co_2$ and 0.0908 of water.

| Calculated for $C_{18}H_{14}O_4$. | Found. |
|---|---|
| C=74·48 % | C=74·40 % |
| H= 3·45 % | H= 3·53 % |

Dicoumarine is an extremely stable compound; it is insoluble in ether, alcohol, and benzol, and dissolves only slightly in chloroform and glacial acetic acid; it is not acted upon at the ordinary temperature by carbonate of soda, ammonia, or caustic soda.

By boiling it for some time with a solution of caustic soda or baryta it slowly dissolves. The solution thus obtained is of a yellow colour, and on the addition of hydrochloric acid the dicoumarine is reprecipitated unchanged. That this is the case is shown by the following analysis:—

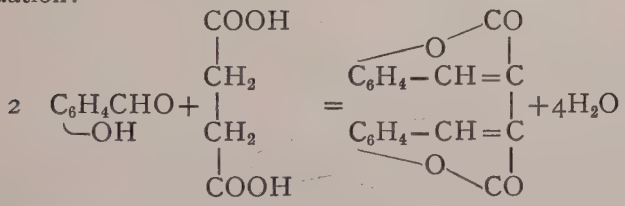
0·220 grammes of substance gave 0·6003 grammes of $CO_2$ and 0·0726 grammes of $H_2O$.

| Calculated for $C_{18}H_{10}O_4$. | Found. |
|---|---|
| C=74·48 % | C=74·45 % |
| H= 3·45 % | H= 3·66 % |

If, however, the hydrochloric acid be gradually added to the alkaline solution, and this be kept cool by surrounding

it with a freezing mixture, a precipitate is obtained which redissolves on addition of sodium carbonate. On attempting to separate this precipitate, by filtration, it is immediately decomposed, dicoumarine being regenerated. It is probable that the body here formed is an unstable oxyacid, incapable of existence at the ordinary temperature, similar, in fact, to that obtained by dissolving coumarine in caustic soda.

The formation of dicoumarine from salicylic aldehyde and succinic acid may be represented by the following equation:—



## Action of Sodium Amalgam on Dicoumarine.

An alkaline solution of dicoumarine, prepared by dissolving dicoumarine in hot concentrated caustic soda and diluting with water, was treated, on the water bath, with sodium amalgam (containing 5 % of sodium) until the precipitate produced by the addition of hydrochloric acid redissolved completely on adding sodium carbonate, thus showing that all the dicoumarine had been reduced.

In order that the reduction may not proceed too slowly it is necessary to keep the solution as nearly neutral as possible without precipitating the dicoumarine. This is done by the occasional addition of hydrochloric acid.

The alkaline fluid, having been decanted from the mercury, was acidified with hydrochloric acid and the precipitate formed collected on a filter. It is not soluble in chloroform or benzol, and only slightly so in ether and water, but dissolves freely in alcohol. It was purified by recrystallisation from dilute alcohol.

The analysis of this body did not lead to any definite formula, and as the results from different experiments were discordant, it seemed probable that the substance, obtained in this manner, was a mixture. Working on this assumption, various methods of separation were tried, and it was finally found, that by conversion into the barium salt, and fractional crystallisation of the same, a separation could be effected.

The mixture was dissolved in a solution of baryta, and the excess of barium precipitated, from the hot solution, by a current of carbon dioxide. On filtering and allowing the filtrate to cool, a barium salt separated out, having the composition $(C_{18}H_{13}O_5)_2Ba + xH_2O$, being in fact barium hydrodicoumarate. In the filtrate there still remained a small quantity of the last-named salt together with a salt much more easily soluble in water. This latter compound is undoubtedly the barium salt of the acid obtained by further reduction of hydrodicoumaric acid.

It was found that when the reduction of the alkaline solution of dicoumarine is only continued until all the dicoumarine is decomposed, very little of this more highly-reduced acid is formed.

## Hydrodicoumaric Acid.

$$C_6H_4-CH=C-CH-CH_2-C_6H_4$$
$$\begin{array}{llllll} | & & | & | & & | \\ O\text{———} & & CO & COOH & & OH \end{array}$$

This acid is obtained as a white precipitate by addition of hydrochloric acid to the solution of the barium salt. It is insoluble in chloroform and benzene, and dissolves only slightly in hot water or ether, but freely in alcohol. By recrystallisation from dilute alcohol it was obtained in needle-shaped crystals.

On heating at 130° C. it is decomposed, without changing its outward appearance, forming an anhydride $C_{18}H_{12}O_4$.

Dried over sulphuric acid (when dried at 100° C. it lost weight, probably due to the formation of a small quantity of the anhydride) it yielded on analysis the following numbers: 0·215 grammes of substance gave 0·5485 grammes of $CO_2$ and 0·0906 grammes of water.

| Calculated for $C_{18}H_{14}O_5$. | Found. |
|---|---|
| C = 69·67 % | C = 69·58 % |
| H = 4·51 % | H = 4·67 % |

---

## Barium Salt.

$$(C_{18}H_{13}O_5)_2Ba + xH_2O.$$

The preparation of this salt has already been described. It is only slightly soluble in cold water, but more readily in hot, from which it separates on cooling in well-defined crystals. These on exposure to the air effloresce and become opaque, rendering it impossible either to determine the water of crystallisation or the crystalline form.

The following are the analytical numbers obtained:—

I. 0·3861 grammes of salt gave on heating at 130° C. 0·04725 grammes of water, and on treatment with sulphuric acid 0·1047 grammes of barium sulphate.

| Calculated on the dried salt. | Found. |
|---|---|
| Ba = 18·18 % | Ba = 18·14% |

The formula $(C_{18}H_{13}O_5)_2Ba + 6H_2O$ requires 12·51% of water. Found 12·2 %.

II. 0·31275 grammes of the salt gave 0·05675 grammes of water, and on treatment with sulphuric acid 0·0787 grammes of $BaSO_4$.

| Calculated on dried salt. | Found. |
|---|---|
| Ba = 18·18 % | Ba = 18·34 % |

Calculated for $(C_{18}H_{13}O_5)_2Ba + 9H_2O = 17·66$ % of water. Found 18·14 %.

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## Silver Salt.

$C_{18}H_{13}O_5Ag$.

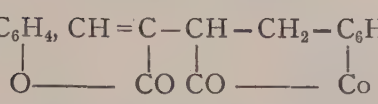
On addition of silver nitrate to a solution of the barium salt, the silver salt was obtained as a white curdy precipitate, which on standing became crystalline. It is almost insoluble in water.

The analysis of the salt, dried over sulphuric acid, gave the following numbers: 0·2325 grammes of the salt yielded 0·4427 grammes of $CO_2$, 0·0687 grammes $H_2O$, and 0·0595 grammes Ag.

| Calculated for $C_{18}H_{13}O_5$ Ag. | Found. |
|---|---|
| C = 52·13 % | C = 51·93 % |
| H = 3·12 % | H = 3·28 % |
| Ag = 25·82 % | Ag = 25·59 % |

The calcium salt, obtained by treating the ammonium salt with calcium chloride, is almost insoluble in water.

## Hydrodicoumarine.



Hydrodicoumaric acid, as has already been mentioned, splits up on being heated at 130° C. into the anhydride, hydrodicoumarine, and water. In order to prepare hydrodicoumarine, hydrodicoumaric acid, which for the purpose need not be quite pure, is melted between watch glasses. The melt, on cooling, is first washed with alcohol, in order to remove any unaltered acid, and then dissolved in hot chloroform; on allowing the chloroform solution to stand hydrodicoumarine is deposited in small but well-defined crystals. It can also be precipitated directly by the addition of alcohol.

Hydrodicoumarine is insoluble in water, alcohol, and ether; it melts at 256° C. and when heated above this temperature sublimes, with partial decomposition, in needle-shaped crystals; the vapour has an odour resembling that of coumarine.

On analysis the following numbers were obtained: 0·2217 grammes of the anhydride, yielded 0·6028 grammes of $CO_2$ and 0·0833 of $H_2O$.

| Calculated for $C_{18}H_{12}O_4$. | Found. |
|---|---|
| C = 73·97 % | C = 74·09 % |
| H = 4·11 % | H = 4·17 % |

In order to see if it could be easily reconverted into the acid, it was boiled with water, in a flask connected with an upright condenser, for three days; at the end of this time it was found to be unaltered. It remains unattacked on

boiling with sodium carbonate or dilute caustic soda, but when heated for some time with strong caustic soda solution, it is reconverted into the acid.

As the crystals of hydrodicoumarine, obtained from its solution in chloroform, were not perfectly satisfactory, it was thought that a better product might be obtained by recrystallising it from dilute acetic acid. Hydrodicoumarine was dissolved in hot glacial acetic acid, and water then added until the precipitate formed just redissolved on boiling. The first crop of crystals not being satisfactory, the process was repeated, and a well-crystallised body was obtained; this on analysis gave the following results:

0·2173 grammes of substance gave 0·5581 grammes of $CO_2$ and 0·091 grammes of $H_2O$.

Calculated for the acid.

| $C_{18}H_{14}O_5$ | Found. |
|---|---|
| C = 69·67 % | C = 70·00 % |
| H = 4·51 % | H = 4·65 % |

From the above results it would follow that, by boiling hydrodicoumarine with acetic acid, hydrocoumaric acid is re-formed. That this is really the case is further shown by the fact that it is almost completely soluble in a solution of carbonate of soda.

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## Action of Bromine on Hydrodicoumaric Acid.

Hydrodicoumaric acid was suspended in chloroform and the calculated quantity of bromine (2 mol. of Br. to 1 of acid) gradually added. It is necessary, in order to prevent

the formation of substitution products, to keep the mixture cool by surrounding it with ice; if this precaution be taken no hydrobromic acid is given off. A clear solution was obtained, from which, on standing, a white precipitate was deposited; it was impossible, however, to isolate this compound, as it immediately decomposed on drying, giving off hydrobromic acid and leaving behind a white insoluble substance. This was purified by dissolving it in hot glacial acetic acid, from which, on cooling, it was deposited in crystals. On analysis the following numbers were obtained:—

0·291 grammes of the substance gave 0·1499 grammes of AgBr.

| Calculated for $C_{18}H_{11}BrO_4$. | Found. |
|---|---|
| Br = 21·56 %. | Br = 21·92 %. |

The compound is consequently monobromhydrodicoumarine. It is soluble in alcohol and ether and dissolves only slightly in chloroform.

In the original solution there still remained a compound which was readily soluble, but has not yet been obtained in the pure state.

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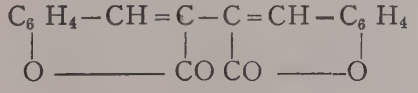
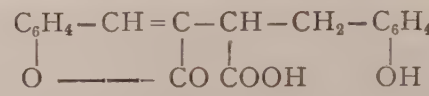
## Theoretical Considerations.

As dicoumarine is formed by the condensation of two molecules of salicylic aldehyde with one of succinic acid, it follows that the simplest constitution that can be given to it is



It has further been shown that by limited reduction, dicoumarine yields a monobasic acid, to which the constitution



has been given.

From this it would appear as if it were necessary, in order for the oxyacid to be stable, that the COOH be combined with a saturated carbon atom. It was, therefore, to be expected that, by further reduction of hydrodicoumaric acid, a dibasic acid would be formed, which should be identical with Zwenger's acid.

---

## Action of Sodium Amalgam on Hydrodicoumaric Acid.

Hydrodicoumaric acid was dissolved in a solution of sodium carbonate and treated repeatedly, on the water bath, with sodium amalgam (containing 5 % of Na). In order to obtain a pure product the reduction must be continued for several days, and the solution kept as nearly neutral as possible. On decanting the alkaline solution from the mercury and acidifying with hydrochloric acid, the new acid was obtained as a white precipitate. This can be purified by recrystallisation from hot water, in which it is only slightly soluble, or from dilute acetic acid.

The best method, however, to obtain it in a perfectly pure state is to convert it into the calcium salt, which can be easily purified by dissolving it in hot water, from which, on cooling, it separates out again in well-defined crystals.

As the calcium salt of hydrodicoumaric acid is nearly insoluble in water, a separation of the two acids can be easily effected.

The new acid, crystallised from dilute acetic acid, forms white crystals easily soluble in alcohol and insoluble in chloroform.

When heated above 100° C. it is slowly decomposed, without changing its appearance, forming an anhydride. The analysis shows it to have the same composition as Zwenger's hydrocoumaric acid $C_{18}H_{18}O_6$, with which, however, it is not identical. This acid may be named "Dihydrocoumaric acid." It forms an insoluble silver salt and a sodium salt readily soluble in alcohol. 0·2216 grammes of the acid yielded 0·5333 grammes of $CO_2$ and 0·1101 grammes of $H_2O$.

| Calculated for $C_{18}H_{18}O_6$. | Found. |
|---|---|
| C = 65·45 % | C = 65·63 % |
| H = 5·45 % | H = 5·52 % |

---

## Calcium Dihydrocoumarate.

$C_{18}H_{16}O_6Ca + 6H_2O$.

This salt was prepared by boiling the acid with water containing calcium carbonate in suspension. On filtering from excess of calcium carbonate and concentrating the filtrate, it separated on cooling, in radiating groups of acicular crystals, containing six molecules of water of crystallisation which it loses on being heated to 140° C.

I. 0·3084 grammes of the salt gave 0·0710 grammes of water, and on addition of sulphuric acid 0·0893 grammes of calcium sulphate.

| Calculated for $C_{18}H_{16}O_6Ca + 6H_2O$. | Found. |
|---|---|
| Ca = 8·40 % | Ca = 8·52 % |
| $H_2O$ = 22·69 % | $H_2O$ = 23·00 % |

II. 0·1616 grammes of salt gave 0·036 grammes of $H_2O$, and 0·0466 grammes of $CaSO_4$.

| Calculated for $C_{18}H_{16}O_6Ca + 6H_2O$. | Found. |
|---|---|
| Ca = 8·4 % | Ca = 8·48 % |
| $H_2O$ = 22·69 % | $H_2O$ = 22·27 % |

---

## Silver Salt.

$C_{18}H_{16}O_6Ag_2$.

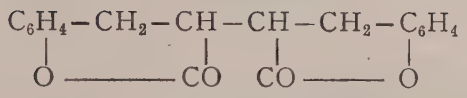
On adding silver nitrate to a solution of the calcium salt (if the ammonium salt be used the product is impure), the silver salt was obtained as a white voluminous precipitate, which on standing became crystalline. The analysis of the salt dried at 100° C. gave the following results: 0·1945 grammes of salt yielded 0·2831 grammes of $CO_2$, 0·0578 grammes of $H_2O$ and 0·0768 grammes of Ag.

| Calculated for $C_{18}H_{16}O_6Ag_2$ | Found. |
|---|---|
| Ag = 39·70 % | Ag = 39·48 % |
| C = 39·70 % | C = 39·76 % |
| H = 2·96 % | H = 3·26 % |

Second determination of the silver: 0·2377 grammes of salt gave 0·0939 grammes of Ag.

| Calculated. | Found. |
|---|---|
| Ag = 39·7 %. | 39·5 %. |

## The Anhydride.



The anhydride was obtained by melting the acid between watch glasses. The melt was then washed with alcohol, in order to remove any undecomposed acid, and dissolved in chloroform; from this solution it separated out on the addition of alcohol, or even on standing, in needle-shaped crystals.

It melts at 222—224° C., and sublimes, with partial decomposition, when heated above this temperature; the vapours possess an odour similar to that of coumarine.

On boiling with water or carbonate of soda it is not altered, but when heated with caustic soda it is slowly dissolved and reconverted into the acid. By fusing with solid caustic soda salicylic acid is formed.

The following are the analytical results obtained:—

0·169 grammes of the substance gave 0·4554 grammes of $CO_2$ and 0·0734 grammes of $H_2O$.

| Calculated for $C_{18}H_{14}O_4$. | Found. |
|---|---|
| C = 73·47 % | C = 73·49 % |
| H = 4·76 % | H = 4·81 % |

This anhydride seems to be identical with that obtained by heating Zwenger's acid, possessing, as it does, the same chemical composition and melting point.

As the properties of the acid, from which the anhydride was prepared, do not correspond with those given by Zwenger for his acid, it was thought desirable to prepare a specimen of the acid, according to his directions, for the sake of comparison.

## Preparation of Hydrocoumaric Acid.

$C_{18}H_{18}O_6$.

20 grammes of coumarine were dissolved in about 50cc. of absolute alcohol and treated repeatedly, on the water bath, with sodium amalgam (containing 5 % of Na). In a short time the insoluble sodium salt separated out in quantity, and this quantity was further increased by the addition of more absolute alcohol.

The salt, after washing with alcohol in order to remove coumarine, sodium coumarate and sodium melilotate, was dissolved in water and this solution acidified with hydrochloric acid; on standing for about two days the acid was deposited in acicular crystals. That this acid is not identical with that obtained by reduction of hydrodicoumaric acid, is shown by the different behavour of the sodium salts towards alcohol; hydrocoumaric acid is also much more readily soluble in water, and the difference between their calcium salts is most marked.

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## Calcium Hydrocoumarate.

$C_{18}H_{16}O_6Ca+2H_2O$.

This salt was prepared by boiling a solution of the acid, in water, with calcium carbonate until no more carbon dioxide was set free. On filtering off the excess of calcium carbonate and concentrating the filtrate, the salt separated out in crystals, containing two molecules of water which was given off on heating at 131—140° C.

Calcium hydrocoumarate dissolves only slightly in either

hot or cold water; if anything, it is rather more soluble in cold than hot. On analysis the following results were obtained :—

0·1167 grammes of the salt on heating at 140° C. gave 0·0101 grammes of $H_2O$ and on addition of $H_2SO_4$ 0·0422 grammes of $CaSO_4$.

| Calculated for $C_{18}H_{16}O_6Ca + 2H_2O$. | Found. |
|---|---|
| $H_2O$ = 8·00 % | $H_2O$ = 7·97 % |
| Ca = 10·00 % | Ca = 9·79 % |

---

## Hydrocoumarine.

$C_{18}H_{14}O_4$.

This was prepared according to the directions given by Zwenger. Hydrocoumaric acid was melted between watch glasses, and the product, on solidifying, washed with alcohol till colourless. It was then dissolved in boiling chloroform, and from this solution it separated out, on the addition of alcohol, in fine acicular crystals. It melted at 222° C., and on analysis gave the following numbers :—

0·2066 grammes of the substance gave 0·5596 grammes of CO and ·09 grammes $H_2O$.

| Calculated for $C_{18}H_{14}O_4$. | Found. |
|---|---|
| C = 73·47 % | C = 73·87 % |
| H = 4·76 % | H = 4·84 % |

The existence of two isomeric acids, having the composition $C_{18}H_{18}O_6$, has, by the above results, been sufficiently proved.

Both these acids, on being heated, yield an anhydride $C_{18}H_{14}O_4$, melting at 222—224°C. Whether the two anhy-

drides are identical or not is at present an open question, the identity of the melting points being possibly a mere coincidence.

By re-converting the anhydrides into acids, and studying the products obtained, there is no doubt but that this question could be satisfactorily settled.

If the anhydrides be found to be identical, we have here another case of isomerism similar to that observed by Perkin* existing between $\alpha$ and $\beta$ coumaric acid; on the other hand, should they prove to be different, hydrocoumaric acid must have a different constitution to that generally assigned to it.

The further investigation of this question is being proceeded with.

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* Jour. Chem. Soc. 39, 409.

## "Curriculum Vitæ."

I, Gibson Dyson, son of John Dyson, was born in Manchester, February 12th, 1863.

I received my early education in private schools, first at Southport and then at Blackpool.

In October, 1880, I was admitted to the Owens College, Victoria University, Manchester, where I studied, under Professors Roscoe, Schorlemmer, Stewart, and Core, until June, 1883.

In October, 1883, I obtained the Dalton Scholarship in Chemistry, which can only be competed for by students of at least three years' standing. During the "Winter Semester," 1883-84, I was at the Polytechnikum, Zürich, working under Professors Meyer and Kenngott.

For the "Summer Semester," 1884, I returned to the Victoria University, Manchester.

In October, 1884, I entered the Kaiser Wilhelm University, Strassburg, where I studied two "Semesters," under Professors Fittig, Kundt, and Bücking.

I here express my gratitude to my former instructors for their ever ready advice and kindness during my term of study.

A. Ireland & Co., Printers, Pall Mall, Manchester.